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ONLINE AUTOMATIC TITRATION OF CHROMIC ACID IN CHROMIUM PLATING SOLUTIONS AND PHOSPHORIC AND SULFURIC ACIDS IN ELECTROPOLISHING SOLUTIONS

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Online Automatic Titration of Chromic Acid In Chromium Plating Solutions And Phosphoric And Sulfuric Acids In Electropolishing Solutions

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Abstract

Two increasingly important issues for the metal finishing industry are product quality and productivity. This industry is constantly looking for better online methods to monitor key chemical components in its metal finishing solutions. The analytical chemistry literature lacks an adequate online automatic titration method for the monitoring of chromic acid in chromium plating solutions and the monitoring of phosphoric and sulfuric acids in electropolishing solutions. Online automatic titration methods for each of these applications are given here based on previous manual titration methods. The identical experiment was conducted at two different companies who sell this type of instrument and included calibration, standardization and analysis. Although this work has a specific objective related to chromium plating and electropolishing solutions, the general method is applicable to most other types of metal finishing solution titrations. The optimum operating range of chromic acid in these chromium plating solutions is 240 - 260 g/l while the optimum respective operating ranges of phosphoric and sulfuric acids are 640 - 730 g/l and 795 - 895 g/l. The resulting online automatic titration precisions for each application equal the present manual titration precisions from which these methods were derived.

Keywords

online chemical analysis, online automatic titration, chromic acid, chromium plating solutions, redox titration, phosphoric acid, sulfuric acid, electropolishing solutions, acid-base titration

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Introduction

Two increasingly important issues for the metal finishing industry are product quality and productivity. This industry is constantly looking for better online methods to monitor key chemical components in its metal finishing solutions. Titration, specifically online automatic titration, is a promising technology toward that goal.

Manual titration is a proven technique for the quantitative determination of most chemical species. There are many general references on this subject (ref 1-8). There are manual chemical analysis methods for chromic acid in chromium plating solutions (ref 9) and for phosphoric and sulfuric acids in electroplating solutions (ref 10). Recently it has become possible to adapt manual titration methods to automated titration methods (ref 11-12). Advantages of automatic titration include reduced operator variability and automatic sampling capability. The online automatic titration methods given here are based on manual ferrous ammonium sulfate titration for chromic acid and manual sodium hydroxide titration with endpoint detection by theoretical endpoint pH values for phosphoric and sulfuric acids.

Theory and Background

The analysis of liquids and solids by either manual or automatic titrimetry is one of the most important and useful methods in analytical chemistry. An explanation of this method is necessary for its evaluation as a chemical analysis technique.

Titration methods of analysis are based on measuring the total capacity of an analyte for a reagent. The three general types of titrimetry are volumetric titrimetry, gravimetric (weight) titrimetry, and coulometric titrimetry. In the first and second types, the volume or weight of a reagent of known concentration is required to react completely with the analyte determined. In coulometric titrimetry, the "reagent" is a constant direct electrical current of known magnitude that reacts directly or indirectly with the analyte where the quantity measured is the time required for quantitative oxidation or reduction of the analyte (ref 2,8).

The basic types of titrations and measuring systems include precipitation-formation, acid-base, complex-formation, oxidation-reduction, photometric, conductometric, coulometric, polarographic, amperometric, and potentiometric methods (ref 1,2,6,8,11,12).

Titration is a quick, accurate, and widely used method for measuring the amount of substance in solution. A standard solution called a titrant is carefully measured by a buret and reacted with an unknown quantity of a second substance. If the volume and concentration of

the titrant are known, the unknown quantity of the substance can be calculated. A titration is based on a chemical reaction that may be represented as:

$$aA + bB \text{ ---> products} \tag{1}$$

where A is the titrant, B is the substance titrated, and a and b are the number of moles of each.

The main requirements of a titration are: 1) the reaction must be stoichiometric where a and b are whole numbers; 2) the rate of chemical reaction must be rapid; 3) the reaction must be 99.9% complete and quantitative when a stoichiometric amount of titrant is added; and 4) a method must be available for determining the point in the titration at which a stoichiometric amount of titrant has been added and the reaction is complete. Experimental detection of this point by an indicator color change or some change in an electrochemical or physical property of the solution is called the endpoint of the titration. The point at which the theoretical amount of titrant has been added is called the equivalence point of the titration. These two points should coincide but may not for various reasons (ref 2,8).

Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 2). Many standard and sample solutions are required. These solutions are prepared or sampled to completely cover the operating ranges of normal production type chromium plating and electropolishing solution concentrations. Two past works by this author (ref 9-10) provide extensive information for preparing, sampling, and chemically analyzing these solutions for all analytes. These analytical chemistry methods are used for quality control purposes for the solutions.

The general type of analytical system used is the online automatic titrimeter which provides chemical analysis of chromic acid in chromium plating solutions and also phosphoric and sulfuric acids in electropolishing solutions. Identical experiments were conducted at Brinkmann Instruments Corporation on its Applikon Model ADI 2000 Automatic Titrimeter System and at Ionics Corporation on its DigiChem Model 3000 Automatic Titrimeter System. They are the only two online automatic titrimetry manufacturers or distributors in the United States.

Each company publishes manuals which are an excellent source of reference for operating conditions, operation and maintenance of these instruments (ref 13-14). The

specifications for each of these instrumental systems include an online automated titrimeter, pH electrode, platinum redox electrode, printer, and computer. The present price of each system is $40,000 to $50,000.

The experimental approach includes calibration and standardization with standard reference chromium plating and electropolishing solutions followed by analysis with sample chromium plating and electropolishing solutions. Calibration and standardization data are used to determine analyte concentrations of sample solutions. All standard and sample solutions are analyzed in triplicate. The acid concentrations in the samples are calculated by normal chemical stoichiometry. Polypropylene and teflon are used throughout these instruments where they come in contact with the sample solutions.

The method used to monitor chromic acid in chromium plating solutions follows.

Two analytical reagent grade standard solutions are required. The first is a 4.90 ± 0.01 g/l potassium dichromate solution that meets American Chemical Society (ACS) Standards and Federal Specification O-C-303D for hexavalent chromium (ref 15-16). The second is a 250 ± 0.1 g/l chromic acid solution that is standardized by the former solution.

One other reagent grade solution is required. It is a redox titrant which has 45.0 ± 0.01 grams of ferrous ammonium sulfate (six hydrate) and 60 ± 1 milliliters of sulfuric acid per liter of total solution.

Preparation of a chromic acid standard for redox titration analysis requires that 0.5 ml of the analytical reagent grade standard solution prepared above is added to the titration vessel by a sampling buret. A buret automatically adds 25 ml of deionized water, 1 ml of concentrated sulfuric acid, and 1 ml of concentrated phosphoric acid. Titrate using the redox titrant, platinum electrode and stirrer to a first derivative endpoint. The endpoint volume is "Reading 1".

Preparation of a chromium plating solution sample for redox titration analysis requires that 0.5 ml of the sample solution is added to the titration vessel by a sampling buret. A buret automatically adds 25 ml of deionized water, 1 ml of concentrated sulfuric acid, and 1 ml of concentrated phosphoric acid. Titrate using the redox titrant, platinum electrode and stirrer to a first derivative endpoint. This endpoint volume is "Reading 2".

The method used to monitor phosphoric and sulfuric acids in electropolishing solutions follows.

Three analytical reagent grade standard solutions are required. The first solution is a 40.00 ± 0.01 g/l sodium hydroxide solution that is standardized with primary standard potassium acid phthalate (ref 6,17). The second is a 4.00 ± 0.05 pH unit standard buffer solution and the third is a 10.00 ± 0.05 pH unit standard buffer solution. These buffer solutions are standardized against primary standard buffer solutions (ref 6).

Preparation of a polishing solution sample for titration analysis requires that 1 ml of sample solution is pipetted into the titration vessel using a sampling buret.

Calibration of the pH electrode is accomplished using both the pH equals 4.00 and 10.00 buffer solutions. The pH readings for each buffer solution may not vary by more than 0.10 pH units.

Titrate using the sodium hydroxide titrant, pH electrode and stirrer to the two theoretical pH endpoints at 4.50 ± 0.10 and 9.70 ± 0.10 pH units. The first and second respective endpoints volumes are "reading A" and "reading B" where "reading B" is the total titrant volume dispensed.

For the chromic acid comparison, Benét Laboratories used 25 ml (manual method) of sample solution per titration while Brinkmann and Ionics used 0.5 ml (online method). For the phosphoric and sulfuric comparison, Benét used 25 ml (manual method) of sample solution per titration while Brinkmann and Ionics used 1 ml (online method). The following applies to each experiment: Each sample solution has three replicate analyses a, b and c. All sample solutions are from actual chromium plating solutions or combinations of these solutions and from actual electropolishing solutions or combinations of these solutions. Sample solution replicates 4d, 4e,4f, 9d, 9e and 9f are from solutions sampled at 130 ± 20° F (54° C) while all other sample solution replicates were from solutions sampled at 72 ± 10° F (22° C). Sample solution temperature does not appear to effect chemical analysis by this method.

Previously the variations in precision were evaluated for the materials and methods used (ref 9-10).

Results and Discussion

Experimental online data is presented in Table 1 for the determination of chromic acid in five chromium plating sample solutions. The redox titration consists of the following equation:

$$(Cr_2O_7)^{2-} + 6(Fe)^{2+} + 14(H)+ \text{<-->} 2(Cr)^{3+} + 6(Fe)^{3+} + 7(H_2O) \qquad (2)$$

All hexavalent chromium is in the dichromate form due to the addition of sulfuric and phosphoric acids as indicated above.

Although all standards and samples are analyzed in their dichromate form, all sample solutions actually contain the chromate form and are reported as chromium trioxide using the following two equations for conversion:

$$(Cr_2O_7)^{2-} + 2(OH)^- \longleftrightarrow 2(CrO_4)^{2-} + H_2O \qquad (3)$$

$$(CrO_4)^{2-} + 2(H)^+ \longleftrightarrow CrO_3 + H_2O \qquad (4)$$

From equations 3-4 it is found that the sodium dichromate standard solution is 245 g/l potassium dichromate or 166.55 g/l chromium trioxide (CrO_3) while the chromic acid standard solution is 250 g/l chromium trioxide (CrO_3).

Therefore, by simple proportion, the calculation for determining the concentration of chromium trioxide in the sample solutions is:

$$\text{g/l } CrO_3 = (250)\frac{\text{Reading 2}}{\text{Reading 1}} \qquad (5)$$

where Reading 2 is the ml of sample titrant and Reading 1 is the ml of standard titrant.

From equation 5, the sample solution chromic acid concentrations and related statistics are calculated and given in Table 1 for Benét, Brinkmann (Applikon) and Ionics.

Experimental online data is presented in Tables 2 and 3 for the determination of phosphoric and sulfuric acids in five electropolishing sample solutions. The acid-base titration consists of the following five equations to various definite extents:

$$H_3PO_4 + NaOH \longleftrightarrow NaH_2PO_4 + H_2O \qquad (6)$$

$$NaH_2PO_4 + NaOH \longleftrightarrow Na_2HPO_4 + H_2O \qquad (7)$$

$$Na_2HPO_4 + NaOH \longleftrightarrow Na_3PO_4 + H_2O \qquad (8)$$

$$H_2SO_4 + NaOH \longleftrightarrow NaHSO_4 + H_2O \qquad (9)$$

$$NaHSO_4 + NaOH \longleftrightarrow Na_2SO4 + H_2O \qquad (10)$$

The calculations for determining the concentrations of phosphoric and sulfuric acids in the sample solutions are:

$$\text{g/l } H_3PO_4 = (B - A)(C)(98)(5) \qquad (11)$$

$$\text{g/l } H_2SO_4 = (2A - B)(C)(49)(5) \qquad (12)$$

where A= Reading A, B= Reading B and C= titrant normality. Reading B is the total titrant volume dispensed and the constant values in equations 11-12 are the combined result of many constants (ref 1,2,6,8).

From equations 11-12, the sample solution phosphoric and sulfuric acid concentrations and related statistics are calculated and given in Tables 2 and 3 for Benét, Brinkmann (Applikon) and Ionics.

Tables 1-3 show that the Ionics and Applikon online concentration means compare well to the Benét offline means. The standard deviation data is reported at both the 68% confidence level (1S= 1 sigma or 1 standard deviation unit) and the 95% confidence level (2S= 2 sigma or 2 standard deviation units). The 95% confidence level is required in order to properly control the concentrations of these three acids in their respective metal finishing solutions. Tables 1-3 show that the Ionics and Applikon online concentration precisions compare well to Benét offline precisions to a 95% confidence level (2S).

Table 4 presents offline laboratory analyses for other important sample solution analytes in the five chromium plating and five electropolishing sample solutions. Chemical analyses of these analytes are by standard offline methods used at Benét (ref 18-20). Since the concentration ranges of each of these analytes spans the operating ranges of these metal finishing solutions, it does not appear that the concentrations of these other analytes effect the chemical analyses of chromic acid in chromium plating solutions or phosphoric and sulfuric acids in electropolishing solutions.

The optimum operating range of chromic acid in these chromium plating solutions is 240 - 260 g/l while the optimum respective operating ranges of phosphoric and sulfuric acids in these electropolishing solutions are 640 - 730 g/l and 795 - 895 g/l. Both online automatic titration methods given here have precisions equal to the present manual laboratory titration methods from which they were derived.

This comparison shows that the online methods are adequate to monitor chromic acid in chromium plating solutions and phosphoric and sulfuric acids in electropolishing solutions. Chemical analysis problems should be minimal since these online methods are similar to the extensively tested offline methods mentioned previously.

Although this technique is being used here only for chromium plating and electropolishing solutions, it is applicable to most chemical species in other metal finishing and associated wastewater solutions. Future use of this technology is already under way toward this goal.

Table 1 - Sample Solutions For Chromic Acid In Chromium Plating Solutions

Sample	Benét (g/l)	Brinkmann (g/l)	Ionics (g/l)
0a	243.8	243.5	243.7
0b	243.6	242.3	243.8
0c	243.8	243.1	243.8
1a	256.3	256.2	256.1
1b	256.1	255.8	256.3
1c	255.9	256.2	256.0
2a	251.2	250.6	251.4
2b	251.6	251.3	251.4
2c	251.6	251.4	251.5
3a	247.5	247.3	247.4
3b	247.5	247.2	247.4
3c	247.6	247.1	247.4
4a	253.4	253.5	253.4
4b	253.1	253.2	253.3
4c	253.5	252.8	253.4
4d	-----	253.1	253.5
4e	-----	253.4	253.4
4f	-----	253.0	253.4
Mean			
0	243.7	243.0	243.8
1	256.1	256.1	256.1
2	251.4	251.1	251.4
3	247.5	247.2	247.4
4 (a-c only)	253.3	253.2	253.4
4 (d-f only)	-----	253.1	253.4
Std Dev (1S)			
0	0.1	0.6	0.1
1	0.2	0.2	0.2
2	0.2	0.4	0.1
3	0.1	0.1	0.1
4 (a-c only)	0.2	0.4	0.1
4 (d-f only)	---	0.2	0.1
worst case (1S)	0.2	0.6	0.2
worst case (2S)	0.4	1.2	0.4

Table 2 - Sample Solutions For Phosphoric Acid In Electropolishing Solutions

Sample	Benét (g/l)	Brinkmann (g/l)	Ionics (g/l)
5a	661.5	662.4	658.8
5b	661.5	658.2	660.6
5c	656.6	662.2	663.7
6a	644.7	646.5	642.9
6b	645.2	647.1	641.5
6c	641.9	644.8	641.0
7a	655.3	653.4	658.2
7b	658.0	656.3	659.6
7c	659.2	655.6	654.7
8a	688.3	691.7	690.5
8b	693.5	687.2	692.9
8c	693.1	690.0	690.5
9a	700.6	696.9	704.0
9b	698.4	699.4	703.7
9c	705.9	699.3	706.6
9d	-----	702.1	699.2
9e	-----	700.3	705.6
9f	-----	696.0	701.0
Mean			
5	659.9	660.9	661.0
6	643.9	646.1	641.8
7	657.5	655.1	657.5
8	691.6	689.6	691.3
9 (a-c only)	701.6	698.5	704.8
9 (d-f only)	-----	699.4	701.9
Std Dev (1S)			
5	2.8	2.4	2.5
6	1.8	1.2	1.0
7	2.0	1.5	2.5
8	2.9	2.3	1.4
9 (a-c only)	3.9	1.4	1.6
9 (d-f only)	---	3.1	3.3
worst case (1S)	3.9	3.1	3.3
worst case (2S)	7.8	6.2	6.6

Table 3 - Sample Solutions For Sulfuric Acid In Electropolishing Solutions

Sample	Benét (g/l)	Brinkmann (g/l)	Ionics (g/l)
5a	762.0	766.2	767.3
5b	764.4	758.7	760.8
5c	770.8	761.9	766.1
6a	852.7	852.9	852.1
6b	846.7	847.0	851.5
6c	851.6	845.2	852.8
7a	801.1	805.7	800.1
7b	796.4	803.8	804.3
7c	803.8	804.4	805.6
8a	815.9	811.5	820.4
8b	815.3	816.5	821.3
8c	812.6	817.3	813.8
9a	826.5	833.5	824.7
9b	826.3	827.0	823.9
9c	829.0	826.6	827.4
9d	-----	830.0	828.4
9e	-----	834.2	828.4
9f	-----	828.1	828.9
Mean			
5	765.7	762.3	764.7
6	850.3	848.4	852.1
7	800.4	804.6	803.3
8	814.6	815.1	818.5
9 (a-c only)	827.3	829.0	825.3
9 (d-f only)	-----	830.8	828.6
Std Dev (1S)			
5	4.5	3.8	3.5
6	3.2	4.0	0.7
7	3.7	1.0	2.9
8	1.8	3.1	4.1
9 (a-c only)	1.5	3.9	1.8
9 (d-f only)	---	3.1	0.3
worst case (1S)	4.5	4.0	4.1
worst case (2S)	9.0	8.0	8.2

Table 4 - Laboratory Analyses For Other Important Sample Solution Analytes

Chromium Plating Sample Solutions	H2SO4 (g/l)	Cr(III) (g/l)	Fe (g/l)
0	2.63	2.4	2.1
1	3.12	0.1	0.2
2	2.95	1.5	3.0
3	2.77	3.9	3.4
4	2.83	2.1	0.8

Electropolishing Sample Solutions	Fe (g/l)
5	2.1
6	5.3
7	4.7
8	1.4
9	0.7

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